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Translator:


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ABSTRACT OF THE DISCLOSURE

[Abstract]

The present invention relates a binder for a lithium-sulfur battery, and the binder includes acrylonitrile-including copolymer.

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The binder exhibits high adherence to positive active materials, and allow for higher relative amounts of positive active materials to be used in the battery resulting in a high capacity lithium-sulfur battery.

[Representative Drawings]

FIG. 1

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[Key words]

Acrylonitrile, binder, lithium sulfur battery

[SPECIFICATION]

[TITLE OF THE INVENTION]

BINDER FOR A LITHIUM-SULFUR BATTERY, POSITIVE ACTIVE MATERIAL
COMPOSITION COMPRISING SAME AND LITHIUM-SULFUR BATTERY USING SAME

[BRIEF DESCRIPTION OF THE DRAWINGS]

FIG. 1 is a graph illustrating charge and discharge characteristics of the lithium-sulfur
cells according to Examples 1 and 2 of the present invention and Comparative Examples 1 and 2.

[DETAILED DESCRIPTION OF THE INVENTION]

[OBJECT OF THE INVENTION]

[FIELD OF THE INVENTION AND THE RELATED ART]

[Field of the Invention]

The present invention relates to a binder for a lithium-sulfur battery, a positive active
material composition comprising the same and a lithium-sulfur battery comprising the same, and
more particularly, to a binder for a lithium-sulfur battery exhibiting good adhesion.

[Description of the Related Art]

The rapid development of smaller, lighter, and higher performance electronic and
communication equipment has required the development of high performance and large capacity
batteries to power such equipment. Lithium-sulfur batteries are of interest because they have
the highest theoretical energy density, 2800Wh/kg (1675mAh/g), as compared to other batteries.
In addition, sulfur is an abundant and inexpensive material, and is also environmentally friendly.
Thus, many researchers attempted rechargeable lithium battery using sulfur.

Because sulfur as a positive active material has no conductivity, it is required to use a
conductive agent to transfer electrons generated during the electrochemical reaction. The
conductive agent may be carbon blacks or metal powders. However, the choice of a binder is

critical for determining battery performance. The requirements for the binder include no reaction with polysulfide, that is, chemical resistance to polysulfide, an ability to enhance the mechanical integrity of the positive electrode, stability at battery working temperatures. Furthermore, the binder has solubility in organic solvents used in slurry, insolubility in electrolytes, and high adherence. However, the requirements cause the limitation of the usable binder so that some materials which satisfy such physical properties rather than the high adherence should be used.

[SUBJECT MATTER OF THE INVENTION]

It is an object of the present invention is directed to a binder for a lithium-sulfur battery exhibiting good adherence..

It is another object to provide a binder for a lithium-sulfur battery having no solubility to an electrolyte, and good resistance to chemicals.

It is still another object to provide a positive active material composition for a lithium-sulfur battery with a low binder content.

It is still another object to provide a lithium-sulfur battery including the binder exhibit a high capacity.

[ELEMENTS AND WORKING EXAMPLES OF THE INVENTION]

To achieve these and other advantages and in accordance with the purpose of the present invention, as embodied and broadly described, the present invention may include a binder for a lithium-sulfur battery wherein the binder comprises an acrylonitrile-including copolymer.

In another aspect of the present invention, the present invention may include a positive active material composition for a lithium-sulfur battery including a positive active material comprising sulfur or a sulfur-based compound, a conductive agent, an organic solvent, and an

agent for controlling viscosity, and an binder which may be present in the organic solvent in the form of emulsion, with a size of about 15 micrometers or less. In certain embodiments, the amount of the binder may range from about 2 to about 6 wt%, and may preferably range from about 2 to about 3 wt%.

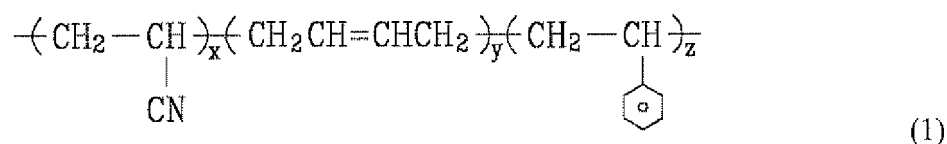
Reference will now be made in detail to an embodiment of the present invention.

The present invention relates to a binder for a lithium-sulfur battery.

The binder includes an acrylonitrile-including copolymer, and the binder is not dissolved in organic solvents, and is a non-aqueous material, preferably distributed in an organic solvent in the form of emulsion.

In accordance with certain embodiments of the present invention, the acrylonitrile-including copolymer is preferably acrylonitrile-butadiene-styrene rubber, acrylonitrile-butadienerubber, or a modified styrene-butadiene rubber, and in certain embodiments, the modified styrene-butadiene copolymer may be carboxylated styrene-butadiene copolymer. An exemplary copolymer that may be used in the present invention is represented by the following

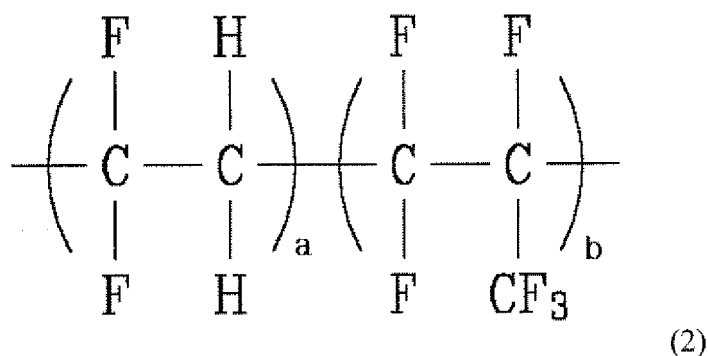
Formula 1.



The “-(CH₂CH=CHCH₂)-“ unit at the center portion of Formula 1 typically imparts rubber-like characteristics to the copolymer, and the “-(CH₂-CHCN)-“ and “-(CH₂-CHC₆H₅)-“ units impart glass-like characteristics to the copolymer. Preferably, the copolymer has a structure where two of x, y, and z cannot be zero. If two of x, y, and z are zero, the resulting polymer typically exhibits relatively poor mechanical properties. In the present invention, the preferred

x, y, and z values depend on the type of copolymer used, and if a styrene butadiene-based copolymer is used, x is zero, y preferably ranges from about 5 to about 40, and z preferably ranges from about 60 to about 95; if an acrylonitrile butadiene-based copolymer is used, x preferably ranges from about 60 to about 95, y preferably ranges from about 5 to about 40, and z is zero; and if an acrylonitrile butadiene styrene-based polymer is used, x preferably ranges from about 20 to about 75, y preferably ranges from about 5 to about 20, and z preferably ranges from about 20 to about 75. If the x, y, and z values exceed the above preferred ranges, the binder will typically display inappropriate mechanical properties.

In another embodiment of the present invention, the binder for the lithium-sulfur battery may further include a fluorine-based polymer. The fluorine-based polymer helps to improve adhesion and to control swelling. An exemplary fluorine-based polymer that may be used in the present invention is represented by the following Formula 2:



(In certain embodiments, a may range from about 0.5 to about 1.0, and more preferably range from about 0.8 to about 1.0 and b may range from about 0 to about 0.5, and more preferably range from about 0 to about 0.2.)

In other embodiments, the fluorine-based polymer may be a homopolymer composed of a monomer selected from the group consisting of $\text{C}_2\text{F}_3\text{Cl}$, $\text{C}_2\text{H}_3\text{F}$, and $\text{CH}_3(\text{CF}_3\text{C}_2\text{H}_4)\text{SiO}$, or the fluorine-based polymer may be a copolymer composed of a first monomer selected from the

group consisting of C_2F_4 , C_2F_3Cl , CH_2CF_2 , C_2H_3F , and $CH_3(CF_3C_2H_4)SiO$, and a second monomer selected from the group consisting of C_2H_4 , C_3H_6 , $CH_2=CHOR$ (where R is a C_1 to C_{20} alkyl group), C_3F_6 , and $CF_2=CFOR_f$ (R_f includes at least 1 fluorine atom and is preferably a C_1 to C_{20} alkyl group with at least 1 and preferably 1 to about 60 fluorine atoms).

5 If the binder uses both an acrylonitrile-including copolymer and a fluorine-based polymer, the ratio of butadiene-based copolymer to fluorine-based polymer may range from about 10% butadiene-based copolymer to about 90 % fluorine-based polymer by weight to a ratio of about 90% butadiene-based copolymer to about 10 % fluorine-based polymer by weight.

The binder may be included in a positive active material composition. In a positive
10 active material composition including the binder, a positive active material, a conductive material, an organic solvent, and an agent for controlling viscosity, the binder is preferably distributed in the organic solvent in the form of an emulsion having a particle size of 15 micrometers or less. Conventional binders are typically presented in the organic solvent in a dissolved state, whereas in certain preferred embodiments, the binder of the present invention is distributed in the organic
15 solvent. The positive active material particles, to be discussed below, more firmly adhere to each other via the distributed binder particles than with a dissolved binder. The adhesion increases as the size of the binder particle becomes smaller, and preferably, the size of the binder particle is about 15 micrometers or less.

The good adhesion characteristics of the binder of the present invention permits a
20 decrease in the amount of binder used in the positive active material composition to 2 to 6 wt%, and preferably 2 to 3 wt% when compared to conventional binders of about 20 wt%. The decreased amount of the binder allows for an increase in the amount of the positive active material in the composition, which results in high capacity lithium-sulfur batteries. The

positive active material composition of the present invention preferably includes an agent for controlling viscosity to offset the decrease in viscosity of the positive active material composition. The agent for controlling viscosity may include a cellulose-based polymer such as methyl cellulose, hydroxypropyl methylcellulose, hydroxyethyl-cellulose, or carboxymethyl cellulose, polyvinyl alcohol, polyvinylpyrrolidone, polyacrylic acid, polyacrylamide, polyethyleneoxide, or polyethyleneimine. In certain embodiments, the amount of the agent for controlling viscosity preferably ranges from about 0.1% to about 10% by weight of the positive active material composition and if the amount of the agent is less than about 0.1% by weight of the positive active material composition, the viscosity of the positive active material composition may be too low to coat on a current collector. If the amount of the agent is more than about 10% by weight of the positive active material composition, the relative amount of the positive active material is reduced, thereby decreasing the capacity of the battery.

The positive active material used in the positive active material composition may include, but is not limited to, elemental sulfur (S_8), Li_2S_n (where $n \geq 1$), an organic-sulfur compound, or a carbon-sulfur polymer $[(C_2S_x)_n]$, where x ranges from about 2.5 to about 50 and $n \geq 2$. The conductive material used in the positive active material composition includes an electrical conductor that facilitates the movement of electrons within the positive electrode with the sulfur-based compound, and examples of the conductive material include, but are not limited to, one or a combination selected from a conductive material such as carbon black, and a conductive polymer such as polyaniline, polythiophene, polyacetylene, polypyrrole, or a combination thereof. The amount of the conductive material preferably ranges from about 5 % to about 20% by weight, and thus the amount of the positive active material increases to a maximum of 92.9% by weight which results in an increase in capacity of the resulting battery.

The organic solvent used in the positive active material composition may be any solvent as long as it is capable of homogeneously dispersing the positive active material, the binder, and the conductive material, and according to certain embodiment, useful solvents include, but are not limited to, acetonitrile, methanol, ethanol, tetrahydrofuran, water, and isopropyl alcohol..

5 The positive active material composition is coated on a current collector and dried to produce a positive electrode. The material for the current collector is not limited, but is preferably made of a conductive material such as stainless steel, aluminum, copper, or titanium, and in certain preferred embodiments, the current collector is a carbon-coated aluminum current collector. The carbon-coated aluminum current collector exhibits excellent adhesive properties to the
10 positive active material composition. Further, the carbon-coated aluminum current collector exhibits a lower contact resistance than a bare aluminum current collector and also inhibits corrosion by a polysulfide compared to a bare aluminum current collector. Using the positive electrode, a negative electrode, and an electrolyte, a lithium-sulfur battery is fabricated by general procedures known to those skilled in the art.

15 Typically, the negative electrode includes a negative active material selected from a lithium metal or a lithium alloy such as lithium/aluminum. In addition, during charging and discharging of the lithium-sulfur battery, the positive active material, active sulfur, converts to an inactive material, inactive sulfur, which can attach to the surface of the negative electrode, and the term "inactive sulfur", as used herein, refers to sulfur that has no activity upon repeated
20 electrochemical and chemical reactions such that it cannot participate in an electrochemical reaction with the positive electrode, and the inactive sulfur on the surface of the negative electrode acts as a protective layer for the lithium negative electrode. Accordingly, inactive sulfur, for example lithium sulfide, on the surface of the negative electrode can be used in the

negative electrode.

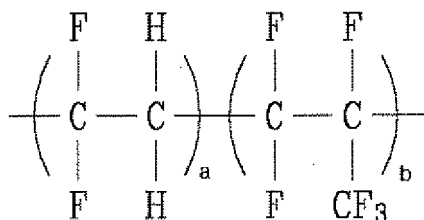
The following examples illustrate the present invention in further detail. However, it is understood that the present invention is not limited by these examples.

Example 1

5 84 wt% of elemental sulfur (S_8), 12 wt% of ketjen black (Mitsubishi), 2 wt% of an acrylonitrile butadiene styrene copolymer binder, and 2 wt% of carboxymethyl cellulose as an agent for controlling viscosity were uniformly mixed in a water solvent. The mixing step was performed until these materials were uniformly mixed, and after mixing, the obtained slurry was coated on a current collector (carbon-coated Al current collector). The coated current collector
10 was dried to produce a positive electrode. Using the positive electrode, a lithium foil negative electrode, a polypropylene separator, and an electrolyte, a lithium-sulfur cell was fabricated in a dry room. The electrolyte was 1M $LiSO_3CF_3$ in a mixed solvent of 1,3-dioxolane/diglyme/sulforane/dimethoxy ethane (5:2:1:2 volume ratio), and the assembly step was performed by positioning the lithium foil, the separator and the positive electrode followed by
15 injecting the electrolyte.

Example 2

84 wt% of elemental sulfur (S_8), 12 wt% of ketjen black (Mitsubishi), 1 wt% of a fluorine-based binder represented by Formula 2, 1 wt% of an acrylonitrile butadiene styrene copolymer binder, and 2 wt% of carboxymethyl cellulose as an agent for controlling viscosity
20 were uniformly mixed in a water solvent to prepare a slurry.



(2)

(wherein a is 0.85, and b is 0.15)

The mixing step was performed until these materials were uniformly mixed, and after mixing, the obtained slurry was coated on a current collector (carbon-coated Al current collector).

The coated current collector was dried to produce a positive electrode.

Using the positive electrode, a lithium foil negative electrode, a polypropylene separator, and an electrolyte, a lithium-sulfur cell was fabricated in a dry room. The electrolyte was 1M LiSO_3CF_3 in a mixed solvent of 1,3-dioxolane/diglyme/sulforane/dimethoxy ethane (5:2:1:2 volume ratio), and the assembly step was performed by positioning the lithium foil, the separator and the positive electrode followed by injecting the electrolyte.

Comparative Example 1

60 wt% of elemental sulfur (S_8), 20 wt% of ketjen black (Mitsubishi), and 20 wt% of polyethyleneoxide were uniformly mixed in an acrylonitrile solvent. The mixing step was performed until these materials were uniformly mixed, and after mixing, the obtained slurry was coated on a current collector (carbon-coated Al current collector). The coated current collector was dried to produce a positive electrode.

Using the positive electrode, a lithium foil negative electrode, a polypropylene separator, and an electrolyte, a lithium-sulfur cell was fabricated in a dry room. The electrolyte was 1M LiSO_3CF_3 in a mixed solvent of 1,3-dioxolane/diglyme/sulforane/dimethoxy ethane (5:2:1:2 volume ratio), and the assembly step was performed by positioning the lithium foil, the separator

and the positive electrode followed by injecting the electrolyte..

Comparative Example 2

60 wt% of elemental sulfur (S_8), 20 wt% of ketjen black (Mitsubishi) and 20 wt% of polyvinylpyrrolidone were uniformly mixed in an acrylonitrile solvent. The mixing step was performed until these materials were uniformly mixed, and after mixing, the obtained slurry was coated on a current collector (carbon-coated Al current collector). The coated current collector was dried to produce a positive electrode.

Using the positive electrode, a lithium foil negative electrode, a polypropylene separator, and an electrolyte, a lithium-sulfur cell was fabricated in a dry room. The electrolyte was 1M $LiSO_3CF_3$ in a mixed solvent of 1,3-dioxolane/diglyme/sulforane/dimethoxy ethane (5:2:1:2 volume ratio), and the assembly step was performed by positioning the lithium foil, the separator and the positive electrode followed by injecting the electrolyte..

The charge and discharge characteristics of the cells according to Examples 1 and 2 and Comparative Examples 1 and 2 were measured at room temperature. The lithium-sulfur battery was initially discharged for 1 cycle at a discharging current density of 0.2 mA/cm^2 , since the test cell had been charged on cell formation. Thereafter, a charge current density was set to 0.4 mA/cm^2 and the discharge current density was set to 0.2 mA/cm^2 (C-rate was 0.1C). The discharge cut-off voltage was set to 1.5~2.8 V. The results are presented in FIG. 1. As illustrated in FIG. 1, although the discharge average voltages of the cells according to Examples 1 and 2 were similar to those according to Comparative Examples 1 and 2, the capacity per gram of electrode of the cells according to Examples 1 and 2 was higher than in Comparative Examples 1 and 2.

[EFFECT OF THE PRESENT INVENTION]

The binder of the present invention exhibits good adhesion to the positive active material, and such good adhesion permits an increase in the amount of the positive active material, which results in providing high capacity lithium-sulfur batteries.

WHAT IS CLAIMED IS:

1. A binder for a lithium-sulfur battery, comprising:

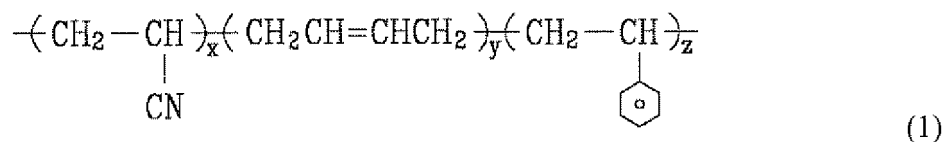
an acrylonitrile-including copolymer.

2. The binder of claim 1, wherein the acrylonitrile-including copolymer is selected

from the group consisting of an acrylonitrile-butadiene-styrene rubber, an acrylonitrile-butadiene rubber, and a modified styrene-butadiene rubber.

3. The binder of claim 1, wherein the acrylonitrile-including copolymer is

represented by Formula 1:



and wherein:

when x is 0, y ranges from about 5 to about 40, and z ranges from about 60 to about 95;

when z is 0, x ranges from about 60 to about 95 and y ranges from about 5 to about 40;

and

when x, y, and z do not equal 0, x ranges from about 20 to about 75, y ranges from about 5 to about 20, and z ranges from about 20 to about 75.

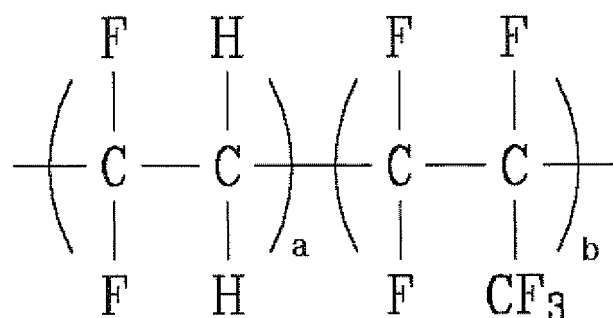
4. The binder of claim 1, wherein the acrylonitrile-including copolymer is a non-

aqueous material.

5. The binder of claim 1, further comprising a fluorine-based polymer.

6. The binder of claim 5, wherein the fluorine-based polymer is represented by

Formula 2:



(2)

and wherein a ranges from about 0.5 to about 1.0, and b ranges from about 0 to about 0.5.

7. The binder of claim 5, wherein the fluorine-based polymer is selected from the group consisting of a homopolymer prepared from monomers selected from the group consisting of $\text{C}_2\text{F}_3\text{Cl}$, $\text{C}_2\text{H}_3\text{F}$ and $\text{CH}_3(\text{CF}_3\text{C}_2\text{H}_4)\text{SiO}$, and a copolymer including a first monomer and a second monomer, wherein the first monomer is selected from the group consisting of C_2F_4 , $\text{C}_2\text{F}_3\text{Cl}$, CH_2CF_2 , $\text{C}_2\text{H}_3\text{F}$ and $\text{CH}_3(\text{CF}_3\text{C}_2\text{H}_4)\text{SiO}$, and the second monomer is selected from the group consisting of C_2H_4 , C_3H_6 , $\text{CH}_2=\text{CHOR}$ where R is a C_1 to C_{20} alkyl group, C_3F_6 and $\text{CF}_2=\text{CFORf}$ where Rf is a C_1 to C_{20} alkyl group with at least one fluorine atom.

8. A positive active material composition for a lithium-sulfur battery, comprising:
a positive active material comprising sulfur or a sulfur-based compound;
a conductive agent;

an organic solvent;

a binder comprising a acrylonitrile-including copolymer, wherein the binder is distributed in the organic solvent to form an emulsion with particle sizes of 15 micrometers or less; and

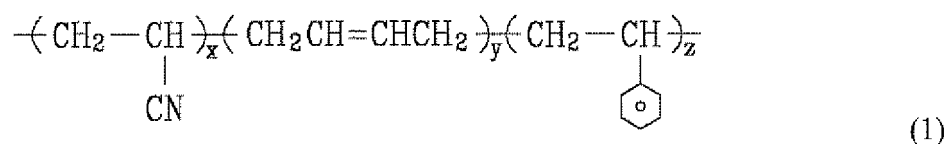
an agent for controlling viscosity.

9. The positive active material composition of claim 8, wherein the binder is presented in the amount of 2 to 6% by weight of the positive active material composition.

10. The positive active material composition of claim 9, wherein the binder is presented in the amount of 2 to 3% by weight of the positive active material composition.

11. The positive active material composition of claim 8, wherein the acrylonitrile-including copolymer is selected from the group consisting of an acrylonitrile-butadiene-styrene rubber, an acrylonitrile-butadiene rubber, and a modified styrene-butadiene rubber.

12. The positive active material composition of claim 8, wherein the acrylonitrile-including copolymer is represented by Formula 1:



and wherein:

when x is 0, y ranges from about 5 to about 40, and z ranges from about 60 to about 95;

when z is 0, x ranges from about 60 to about 95 and y ranges from about 5 to about 40;
and

when x, y, and z do not equal 0, x ranges from about 20 to about 75, y ranges from about 5 to about 20, and z ranges from about 20 to about 75.

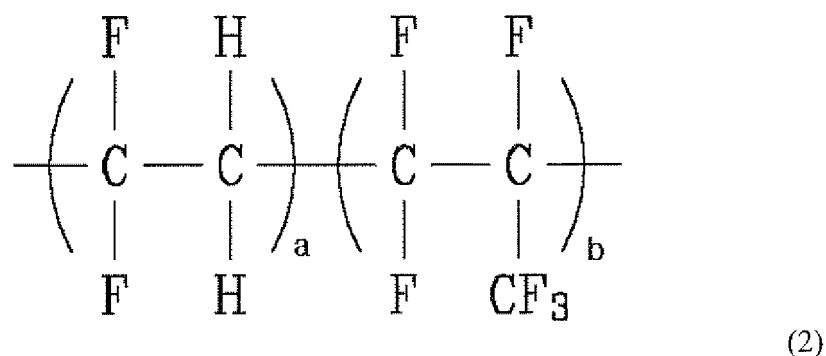
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13. The positive active material composition of claim 8, wherein the acrylonitrile-including copolymer is non-aqueous.

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14. The positive active material composition of claim 8, further comprising a fluorine-based polymer.

15. The positive active material composition of claim 14, wherein the fluorine-based polymer is represented by Formula 2:



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and wherein a ranges from about 0.5 to about 1.0, and b ranges from about 0 to about 0.5.

16. The positive active material composition of claim 14, wherein the fluorine-based polymer is selected from the group consisting of a homopolymer prepared from monomers

selected from the group consisting of C_2F_3Cl , C_2H_3F and $CH_3(CF_3C_2H_4)SiO$, and a copolymer including a first monomer and a second monomer, wherein the first monomer is selected from the group consisting of C_2F_4 , C_2F_3Cl , CH_2CF_2 , C_2H_3F and $CH_3(CF_3C_2H_4)SiO$, and the second monomer is selected from the group consisting of C_2H_4 , C_3H_6 , $CH_2=CHOR$ where R is a C_1 to C_{20} alkyl group, C_3F_6 and $CF_2=CFOR_f$ where R_f is a C_1 to C_{20} alkyl group with at least one fluorine atom.

17. A lithium-sulfur battery, comprising:
a binder comprising an acrylonitrile-including copolymer;

FIG

FIG. 1

